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TITLE: POLYLACTIC ACID COMPOSITION, PRODUCTION THEREOF,  
AND  
MOLDED ARTICLE PREPARED THEREFROM

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ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a polylactic acid compsn. which does not

require a posttreatment after polymn., is excellent in heat stability, and does not exhibit the mol.wt. decrease or discoloration in molding by subjecting a lactide of a cyclic dimer of lactic acid (L-isomer and/or D-isomer) alone or together with a polyhydric alcohol, a lactone, etc., to ring-opening polymn. in the presence of a polycarboxylic acid.

SOLUTION: Pref., triacetylacetonatoaluminum in an amt. of 0.3-3 mol% based on a lactide is used as the catalyst for producing polylactic acid, and the use of tin octoate in an amt. of 0.003-0.0001 mol% together with the above compd. is pref. A polycarboxylic acid to be incorporated into polylactic acid is e.g. oxalic acid, succinic acid, or terephthalic acid, citric acid being esp. pref., and the amt. of it incorporated is pref. 0.001-1 wt.% of the lactide. The polymn. is conducted pref. at the m.p. of the resultant polymer or higher but not higher than 200°C and in an anhydrous atmosphere. A copolymer mainly comprising lactic acid can also be used as polylactic acid.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention -- the object for garments -- Japanese -- business -- it is related with the Plastic solid which consists of the powder and fiber which can be used for industrial materials, such as the object for a life, the object for drugs ingredients, an object for medical ingredients and agriculture, a fishing, industry, and construction engineering works, a film and a polylactic acid constituent suitable as a molding material, its manufacture approach, and this constituent.

[0002]

[Description of the Prior Art] Polylactic acid attracts attention from a viewpoint of earth resource protection to the synthetic polymer of the conventional petroleum origin in order to use as a raw material the lactic acid which grain is fermented and is obtained. Moreover, since hydrolyze comparatively easily in underwater and the living body, it exists in a nature widely among soil, it becomes a harmless lactic acid to animals and plants and it is finally decomposed into a carbon dioxide and water by a metabolic turnover or microbial degradation, polylactic acid attracts attention also as a biodegradability ingredient. Furthermore, since the safety to a living body is high, application to physic and the medical field is performed briskly especially in recent years.

[0003] As a synthesis method of polylactic acid, after oligomerizing a lactic acid, this is depolymerized and the approach of isolating the lactide which is an annular dimer, making carry out ring opening polymerization of this lactide, and acquiring is learned. Since the polylactic acid of the amount of macromolecules will be obtained comparatively easily if even a deed fully carries out purification of a lactide, this approach is a very useful approach.

[0004] Although the solution polymerization in the inside of a solvent is also possible for manufacture of the polylactic acid by this lactide ring opening polymerization, a great quantity of facilities are required, and since it is difficult, it is industrially more desirable [ the melting polymerization in a non-solvent ] to remove completely the solvent used from the polymerization product which a manufacturing cost also turns high up and was obtained. In the case of a melting polymerization, it is necessary to make the temperature conditions of a polymerization reaction higher than the melting point of the polylactic acid generated from stirring of a system, or the point of the ejection after a polymerization for example, and when it is the Pori L lactic-acid homopolymer, it is required to be 180 degrees C or more.

[0005] On the other hand, it is already known that various metallic compounds have a catalysis in this lactide ring opening polymerization, and improvement in a rate of polymerization is achieved by that use. It is especially used for the height of catalytic activity [ octylic acid tin (it is hereafter written as Sn (Oct)<sub>2</sub> ) ], and FDA (Food and drug administration: U.S. Food and Drug Administration) preferably from the point that the use is approved as a stabilizer etc.

[0006]

[Problem(s) to be Solved by the Invention] Originally polylactic acid is a transparent and colorless polymer, and the application in which the property was harnessed is possible for it. However, in order to obtain the polylactic acid which does not have coloring in order to color it yellow, if polylactic acid is set in the state of melting for a long time, it is necessary to perform a polymerization and fabrication promptly. Above-mentioned Sn<sub>2</sub> (Oct) In order to complete a polymerization within dozens of minutes at 180 degrees C if it is mostly used from 0.003-mol % to a lactide in using as a polymerization catalyst, it hardly colors. However, Sn<sub>2</sub> of the amount of above (Oct) If it remains in a polymer, in order that this may act as a decomposition catalyst of polylactic acid at the time of fabrication and may reduce molecular weight remarkably at it, mold goods with sufficient reinforcement are not obtained. So, in the present condition, it is a polymerization product to Sn (Oct)<sub>2</sub> with approaches, such as reprecipitation or washing, after a polymerization. Although the method of removing is taken, there is a trouble that a process becomes complicated and a manufacturing cost also becomes high.

[0007] Moreover, Sn<sub>2</sub> (Oct) Although the thermal stability of the obtained polylactic acid will improve and the molecular weight fall at the time of molding will decrease if the amount used is reduced even less than [ 0.003 mol % ] to a lactide, polymerization time amount is needed 100 minutes or more at 180 degrees C, and the coloring at the time of a

polymerization is not avoided.

[0008] On the other hand, this invention person etc. has found out that the polylactic acid obtained previously, using tris acetylacetonate aluminum (it being hereafter written as aluminum (Acac)<sub>3</sub>) as a catalyst is very excellent in thermal stability. however, aluminum (Acac)<sub>3</sub> Sn (Oct)<sub>2</sub> if compared -- catalytic activity -- small -- a lactide -- receiving -- several -- about mol % -- since the polymerization time amount for 100 minutes or more is needed at 180 degrees C even if it is used, the coloring at the time of a mist [ this ] beam polymerization is not avoided.

[0009] Therefore, the polylactic acid obtained from the approach of being lactide melting ring opening polymerization with the highest industrial utility value in respect of a manufacturing cost, and having no after treatment after a polymerization is holding the opposite trouble of thermal stability and coloring. This invention aims at offer of the Plastic solid which consists of the new manufacture approach of the polylactic acid constituent which is excellent in thermal stability and does not have coloring that it is made in view of the above-mentioned actual condition, and the molecular-weight fall at the time of shaping does not need the after treatment after a polymerization in the polylactic acid constituent which does not have coloring small, and lactide melting ring opening polymerization, and this polylactic acid constituent.

[0010]

[Means for Solving the Problem] The polylactic acid with which this invention for attaining the above-mentioned purpose consists of L- and/or D-lactic acid, Or L- and/or D-lactic acid and a polyalkylene glycol, polyhydric alcohol, Hydroxycarboxylic acid, aliphatic series polyester, lactone, a lactam, And it consists of the polylactic acid and the multi-base carboxylic-acid compound which are a copolymer with the segment which originates in a kind of compound chosen from the group which consists of annular carbonate at least. further -- aluminum (Acac)<sub>3</sub> or the lactic-acid unit of this polylactic acid -- receiving -- 0.00005-0.0015-mol % of Sn<sub>2</sub> (Oct) from -- it is characterized by the becoming polylactic acid constituent.

[0011] Moreover, the lactide whose invention of a paralysis convex it is and is the annular dimer of a lactic acid, Or this lactide, a polyalkylene glycol, polyhydric alcohol, Hydroxycarboxylic acid, aliphatic series polyester, lactone, a lactam, And it faces manufacturing polylactic acid by carrying out melting ring opening polymerization of a kind of compound chosen from the group which consists of annular carbonate at least. a multi-base carboxylic-acid compound is lived together -- making -- further -- as a catalyst -- aluminum (Acac)<sub>3</sub> or this lactide -- receiving -- 0.0001-0.003-mol % of Sn<sub>2</sub> (Oct) It is the manufacture approach of the polylactic acid constituent characterized by using.

[0012] Furthermore, the polylactic acid with which one invention consists of L- and/or D-lactic acid now Or L- and/or D-lactic acid and a polyalkylene glycol, polyhydric alcohol, Hydroxycarboxylic acid, aliphatic series polyester, lactone, a lactam, And it consists of the polylactic acid and the multi-base carboxylic-acid compound which are a copolymer with the segment which originates in a kind of compound chosen from the group which consists of annular carbonate at least. further -- aluminum (Acac)<sub>3</sub> or the lactic-acid unit of this polylactic acid -- receiving -- 0.00005-0.0015-mol % of Sn<sub>2</sub> (Oct) from -- it is the Plastic solid which consists of a becoming polylactic acid constituent.

[0013]

[Embodiment of the Invention] The lactide used for this invention is the annular dimer of the lactic acid obtained by depolymerizing after oligomerizing a lactic acid, as mentioned above. L-lactic acid and D-lactic acid exist in a lactic acid, and L bodies, D object, a meso object, and racemic modification exist also in a lactide in connection with it. The melting point of the amount polylactic acid of macromolecules obtained is determined by the optical purity of polylactic acid, and since high-melting polylactic acid is obtained, if the thing of a high grade desires heat-resistant high polylactic acid more more, it will be desirable [ a thing ], although especially the optical purity of the lactide used for this invention is not limited to use the lactide of the Takamitsu study purity.

[0014] In order that the compound which has a hydroxyl group in the ring opening polymerization of a lactide may work as an initiator of a polymerization, the molecular weight of the polylactic acid to generate is determined by the hydroxyl-group concentration in a polymerization raw material. For example, in the case of a homopolymer, in order to obtain with a weight average molecular weight of 200,000 or more polylactic acid, the moisture content in a raw material lactide needs to be within the limits of 5 ppm - 60 ppm. Moreover, the polymerization degree of the polylactic acid which in the case of a copolymer the molecular weight of the polylactic acid obtained also with the hydroxyl equivalent and loadings of the comonomer used in addition to a moisture content is influenced, and a hydroxyl equivalent blends a small thing so much, namely, is obtained, so that the hydroxyl-group concentration in a polymerization raw material becomes large becomes small.

[0015] Although the multi-base carboxylic-acid compound used in this invention is a compound which contains two or more carboxyl groups in a monad and oxalic acid, a succinic acid, a malonic acid, tricarballic acid, a citric acid, a tartaric acid, a terephthalic acid, etc. are mentioned as such a thing, especially a citric acid is used preferably. Although especially the addition is not specified, it is 0.001 % of the weight - 0.1 % of the weight more preferably so much at the lactide of a raw material 0.0001 % of the weight to 1% of the weight.

[0016] As a catalyst preferably used in the manufacturing method of the polylactic acid constituent of this invention, it is aluminum (Acac)<sub>3</sub> first. It is mentioned. The polylactic acid constituent obtained using this catalyst is very excellent in

thermal stability. aluminum (Acac)<sub>3</sub> in this invention the amount of the catalyst used -- a lactide -- receiving -- desirable -- 0.15-5-mol % -- it is 0.3-3-mol % more preferably. Although the polymerization degree of the polylactic acid which will be obtained if less than [ 0.15 mol % ] is not enough as the polymerization degree of the polylactic acid obtained and the amount used increases increases, thermal stability tends to fall, the increment in polymerization degree is saturated near 3-5 mol %, and polymerization degree falls rather more than by it.

[0017] moreover, the catalyst preferably used next in manufacture of the polylactic acid constituent of this invention -- Sn (Oct)<sub>2</sub> it is -- although -- the amount used is limited severely in this case. This is Sn (Oct)<sub>2</sub>, as mentioned above. In order to use without adding purification actuation of reprecipitation, washing, etc. for a polymerization product since it has high catalytic activity to disassembly of polylactic acid, it is Sn (Oct)<sub>2</sub>. As for the amount used, it is indispensable that it is less than [ 0.003 mol % ] to a lactide. If [ than this ] more, since decomposition progresses and polymerization degree falls remarkably at the time of next fabrication, a product with sufficient reinforcement will not be obtained. Moreover, less than [ 0.0001 mol % ], the effectiveness of the catalyst in a polymerization is hardly seen.

[0018] Although especially the polymerization temperature in this invention is not limited, for the homogeneity of a polymerization, stirring actuation is required, and, as for the minimum of polymerization temperature, for that purpose, it is desirable that it is more than the melting point of the obtained polymerization product. For example, in the case of the Pori L lactic-acid homopolymer, it is desirable that it is 180 degrees C or more. Moreover, as for the upper limit of polymerization temperature, it is desirable that it is 200 degrees C. Since a degree of polymerization stops being able to go up this easily since the polymerization equilibrium of a lactide and a polymer inclines toward a lactide side at an elevated temperature from 200 degrees C, and the amount of generation of a lactide increases, polymer yield falls.

[0019] Moreover, since the time amount which a polymerization takes changes with classes, amounts, etc. of a comonomer when it is the amount of the catalyst used although it was usually 60 - 6000 minutes, polymerization temperature, a moisture content in a system, and a copolymer, it should just choose suitably the time amount which reaches desired polymerization degree. Moreover, it is because of the polymerization degree of the polylactic acid which generates this reaction with the moisture content in a system being influenced as mentioned above. As for the system of reaction, it is desirable that it is under an anhydrous ambient atmosphere, and it is desirable to carry out a polymerization under inert gas ambient atmospheres, such as nitrogen and an argon, or reduced pressure. Moreover, it is also possible to remove a residual lactide by holding and carrying out solid state polymerization of the reaction termination postpolymerization product to a 110-140-degree C temperature requirement.

[0020] This invention can apply not only a polylactic acid homopolymer but a lactic acid also in the various copolymers used as a principal component. That is, it becomes possible to adjust the crystallinity of the polylactic acid obtained combination and by carrying out copolymerization in other monomers, and a biodegradation rate and heat flow rate kinesis. It is also possible for a polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic series polyester, lactone, a lactam, and annular carbonate to be mentioned as a monomer with such effectiveness, and to use two or more kinds of compounds for coincidence.

[0021] As a polyalkylene glycol, for example, homopolymers, these copolymers, etc., such as ethylene glycol and propylene glycol As polyhydric alcohol, ethylene glycol, propylene glycol, Neopentyl glycol, a glycerol, trimethylol propane, etc. As hydroxycarboxylic acid, a glycolic acid, 3-hydroxybutyric acid, As aliphatic series polyester, a 3-hydroxy valeric acid etc. the homopolymer of said hydroxycarboxylic acid and a copolymer, or the polymer of various aliphatic series diols and aliphatic series dicarboxylic acid As lactone, gamma-butyrolactone, beta-valerolactone, epsilon-caprolactone, Glycolide etc. is not limited to this, although gamma-butyrolactam, beta-valerolactam, epsilon caprolactam, etc. can be mentioned as a lactam and propylene carbonate etc. can be mentioned as annular carbonate.

[0022] The mold goods of this invention are mold goods which carry out melting shaping of the polylactic acid constituent of this invention like the above-mentioned, and change. As an example of said mold goods, although the fiber structure objects (knitting, textiles, a nonwoven fabric, paper, a string, a tape, a rope, network, etc.) from said fiber and the composite of said film and sheet still like synthetic leather, and fiber are mentioned further, they are not various mold goods, such as injection and extrusion, a film, a sheet, un-extending or the fiber carried out extension orientation, and the thing limited to this.

[0023] As an application of these mold goods, insect control, incubation, frost prevention, protection from light, the film for weed preventing, Industrial use applications, such as applications for agriculture, such as a sheet and a fiber structure object, and interior of a vehicle, an electric product, The building use of engineering-works applications, such as a sheet for slope vegetation protection, a floor, a wallplate, etc., a disposable instrument, Although applications for fishings, such as a health medical-application way including a \*\* implement including the subsistence store for days and toy including disposable garments, shoes, a bag, etc., a game machine, etc., sanitary items, etc., a fishing net, a fishing line, various ropes for culture, and a network, etc. are mentioned, it is not the object limited to these.

[0024]

[Example] Hereafter, this invention is explained in full detail according to an example. In addition, the measuring method of the various characteristic values in this specification is described before that.

[0025] The weight average molecular weight (it is hereafter written as Mw) of the polymer section was measured by GPC (gel permeation chromatography) which made <weight-average-molecular-weight> chloroform the eluate. In addition, the molecular-weight calibration curve was created using polystyrene.

[0026] For the purpose of <thermal stability appraisal method> thermal stability evaluation, melting processing according a polylactic acid constituent to fixed condition heating was performed. Reduced pressure drying of the sample was carried out at the room temperature under phosphorus pentoxide existence for 24 hours, the about 3g was put into the test tube, and it heated all over the 180-degree C oil bath after the nitrogen purge for 1 hour. That to which the thermal stability which measures Mw polylactic acid constituent's melting processing before (before a polymerization) and after melting processing (after melting) by the above-mentioned approach, and is called for by the following formula exceeds 70% was judged to be the polylactic acid constituent excellent in thermal stability.

$$\text{Mw}(\text{after polymerization}) \times 100 \text{ of Mw}(\text{after melting}) / \text{polylactic acid constituent of a thermal stability (\%)} = \text{polylactic acid constituent}$$
 [0027] With the press machine with a hot-platen temperature of 180 degrees C, to the thickness of 2mm, heating pressurization was carried out, and the polylactic acid constituent obtained by the <coloring nature appraisal method> polymerization was taken out after that, and was quenched. The obtained sample was placed on white paper and viewing estimated the coloring nature.

[0028] (Example 1) L-lactide (moisture-regain [ of 10 ppm ], product made from PURAC) 60g (416mmol), aluminum (Acac)<sub>3</sub> 0.675g (2.08mmol), and 0.06g of citric acids were supplied to the reaction container equipped with stirring equipment and nitrogen installation tubing, and ring opening polymerization was heated and carried out to 180 degrees C under the nitrogen air current after the nitrogen purge. 0.5-mol % and the citric acid of the amount of aluminum (Acac)<sub>3</sub> which is a catalyst at this time were 0.1 % of the weight similarly to L-lactide of a raw material. When the rise of molecular weight was saturated, the reaction was ended and the polymerization product was taken out out of the system. The property of the obtained polylactic acid constituent was as being shown in Table 1. The obtained polylactic acid constituent was colorlessness, and thermal stability became 87.1% from Mw318,000 after a polymerization, and Mw277,000 after melting processing, and it excelled in thermal stability very much.

[0029] (Example 1 of a comparison) The polylactic acid constituent was obtained like the example 1 except not using a citric acid in an example 1. Various characteristic values were as being shown in Table 1, and although thermal stability was excellent, the polylactic acid constituent colored light yellow was obtained.

[0030] (Example 2) aluminum<sub>3</sub> in an example 1 (Acac) It changes and is 0.002-mol % of Sn<sub>2</sub> (Oct) to this lactide. The polymerization was performed like the example 1 except having used as a catalyst. The various characteristic values of the obtained polylactic acid constituent are as being shown in Table 1, and the polylactic acid constituent which excelled [ colorlessness ] in thermal stability was obtained.

[0031] (Example 2 of a comparison) The polylactic acid constituent was obtained like the example 2 except not using a citric acid in an example 2. Various characteristic values were as being shown in Table 1, and although thermal stability was excellent, it became the product colored light yellow.

[0032]

[Table 1]

		実施例 1	比較例 1	実施例 2	比較例 2
触媒 触媒量 : mol %		Al (Acac) <sub>3</sub> 0.5		Sn (Oct) <sub>2</sub> 0.002	
クエン酸添加量 Wt %		0.1	0	0.1	0
着色性		無色	淡黄色	無色	淡黄色
Mw × 10 <sup>4</sup>	重合後	31.8	37.8	27.4	26.8
	熔融後	27.7	32.5	20.9	21.0
熱安定性 (%)		87.1	86.9	76.3	78.4

[0033] (Example 3) The polymerization was performed like the example 1 except having used polyethylene-glycol

PEG6000 (moisture regain of 52 ppm) 2.4g as a polymerization raw material in the example 1 in addition to L-lactide. The various characteristic values of the obtained polylactic acid constituent were as being shown in Table 2, and although polymerization degree was low compared with the homopolymer, the polylactic acid constituent which excelled [ colorlessness ] in thermal stability was obtained.

[0034] (Example 3 of a comparison) The polymerization product was obtained like the example 3 except not using a citri acid in an example 4. Various characteristic values were as being shown in Table 2, and although thermal stability was excellent, it became the product colored light yellow.

[0035]  
[Table 2]

		実施例 3	比較例 3
触媒 触媒量 : mo l %		A l ( A c a c ) , 0 . 5	
クエン酸添加量 W t %		0 . 1	0
着色性		無色	淡黄色
Mw × 1 0 <sup>4</sup>	重合後	1 1 . 4	1 3 . 1
	熔融後	1 0 . 1	1 1 . 7
熱安定性 (%)		8 8 . 6	8 9 . 3

[0036]  
[Effect of the Invention] Since the polylactic acid constituent of this invention is excellent in thermal stability, its fall of molecular weight is small at the time of fabrication, and the product of high intensity can be obtained. Moreover, since there is no coloring, this constituent is applicable suitable for fiber, various films, etc. for garments. Moreover, since it uses lactide melting ring opening polymerization, and the polylactic acid of the amount of macromolecules is obtained easily and the approach of this invention does not need tail end processes, such as removal of a solvent, its industrial valu is very high. further -- the mold goods of this invention -- high intensity -- since [ and ] there is no coloring -- the object for garments -- Japanese -- business -- it is very suitable as the powder used for industrial materials, such as the object for a life, the object for drugs ingredients, the object for medical ingredients and agriculture, a fishing, industry, construction, and engineering works, fiber, a film, a molding material, etc.

[Translation done.]